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IOP Multifunctional Materials - INVITED TOPICAL REVIEW

Temporary tattoo as unconventional substrate for conformable and transferable electronics on skin and beyond

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Abstract

In the growing field of conformable electronics, among the various approaches so far, tattoo technology has emerged. Here temporary tattoo paper is adopted as unconventional substrate to build up transferable body compliant devices, which establish a stable and long-lasting interface with the skin. Tattoo-based devices have shown their capabilities in multiple fields, with main application in human health biomonitoring. Such approach is advancing the state-of-the-art, overcoming some limits of existing technologies, as in the case of skin-contact electrodes and sweat analysis. Temporary tattoo has also been adopted in other fields as in organic electronics, within the development of organic solar cells and transferable edible transistors. Multiple and complementary fabrication approaches on temporary tattoos have been demonstrated, spanning from traditional vacuum-based deposition methods to various printing technologies. In this review, together with reporting and discussing the main fabrication methods and applications of tattoo technology, we describe the main features of the

tattoo substrate. New insights on its material composition and properties are given, discussing the pros and cons in comparison with other approaches adopted in conformable electronics. Together with providing a comprehensive and up to date review of advancements in tattoo technology, this review aims to contribute to ain a better understanding of the capabilities offered by such low cost and versatile substrate. This can help in opening up new research for emerging applications, like in the relevant field of sustainable electronics.

1. Introduction

Recent advancements in materials science and nanotechnology have led to novel approaches toward electronic devices, especially as regards their integration and interface with the human body. Driven also by the increasing demand for wearables and novel biodiagnostic tools, devices have become progressively thinner and softer, with a corresponding shift of attention from the so-called flexible electronics to the new paradigm of epidermal or tattoo electronics. Indeed, as advanced interfacing with the human body is considered, multiple requirements and new challenges come into play. These are not always and not optimally addressable by flexible electronics. Among others, biocompatibility, safe operation on body and unperceivability to the user are the main ones.

The emerging area of epidermal electronics (1) refers to conformable devices which are able to withstand bending to extremely small radii and stretching without impairment of their integrity and functionality. In this way they can adapt to micrometric topography features and adhere seamlessly to the target surface (as the human body). Such performances are obtained thanks to novel materials, fabrication and transfer strategies, reduced thickness and innovative designs. Crucial in this respect is the capability to embed the necessary functions (sensing, elaboration, powering, among others) into thin film materials with minimal or even no mechanical support by a substrate (to minimize stiffness and weight). Materials are intrinsically endowed with proper means of adhesion to target surfaces, as in the case of physical adhesion to skin by Van der Waals forces. In such a way a device can be transferred and can conformally adhere to complex-shaped surfaces, such as the human skin or other biological tissues. Nonetheless, extending the concept of conformable electronics into other scenarios, other biological or non-biological target surfaces are considered for some selected emerging applications, such as structural health monitoring and crops monitoring.(2,3)

A large number of conformable electronics applications has been so far envisioned and proposed. Among others, wearable electronics (4) and various bio-electronics applications.(1) The latter include both conformable implantable devices and surface (skin-mounted) ones with multiple purposes: from monitoring of physical and biochemical parameters for personalized healthcare, to localized and controlled drug-delivery and human-machine interface.(5–11) Efforts in these directions comprise very different approaches in terms of materials and fabrication strategies. They include embedding of rigid, silicon-based micromachined components in stretchable elastomers films,(1,12) as well as organic electronics approaches. Here, organic conductors and semiconductors are deposited (sometimes printed) onto thin or ultrathin polymeric films for developing various active and passive components, including solar cells, organic light emitting diodes (OLEDs), organic field effect transistors (OFETs),(13) as well as various bioelectronic devices.(14,15) Progresses in wearable sensing on the skin (or "lab on skin") have been summarized in some recent critical reviews.(16–19)

In the quest for optimal substrates and transfer strategies for conformable electronics, some research groups took in consideration an "unusual" substrate: a water slide decal transfer paper, better known as temporary tattoo (TT) paper. Decal transfer paper is indeed a printable material enabling to gently but firmly transfer a drawing onto skin or other surfaces, mainly for decorative purposes. TT paper has been in use for decades as a gadget or toy for kids, or also as a tool for make-up and special FX in movies. The transfer on skin is very easy: by soaking with water the back part of decal paper and pressing against skin for some seconds the drawing simply detaches from a support paper sheet and adheres to the skin.

TT paper is extremely cheap, mass produced and readily available in large formats. Because of its facile manipulation, storage and broad processability, it is easy to envision its scaling-up adoption in device fabrication without the use of demanding facilities. Besides being a skin-contact benign material, TT has also a low environmental footprint, the latter being a main advantage in the forthcoming era of ubiquitous and ideally transient electronics.(20,21)

Our group has been working on the development of polymeric conformable substrates for many years. Ultrathin free-standing nanofilms of conjugated polymers were studied (22,23) with various applications in sensing and actuation.(24,25) In the next few years we introduced TT paper as an unconventional substrate for the development of conformable electronics for skin-contact purposes.(26)

Aims of this paper are to introduce the challenges and opportunities offered by a TT paper as a suitable substrate for conformable electronics and to review the main strategies which enabled its adoption in the field. The composition, structure and properties of decal transfer paper will be described in Section 2, highlighting how these features are relevant for developing a skin-mountable and conformable device. In

Section 3 materials processing methodologies implemented so far on tattoo paper will be reviewed. Section 4 will then review examples of recent literature for several classes of electronic components on TT paper, as used into various application domains. Section 5 summarizes future prospects and emerging fields of applications of TT devices, even beyond skin or the human body.

2. Temporary Tattoo Paper: structure and features

TT paper is a type of water slide decal. Decals (short from “decalcomania”) were first invented in late 1700 and have been in use in transfer printing since more than a century for decorative purposes, mainly for pottery ornament on mass scale. This technique allows to transfer a thin printed pattern to another surface upon contact. Usually heat or water is applied for enabling the transfer. In a water slide decal the “transfer” (printed pattern/image to be transferred) is deposited during production onto a water soluble sacrificial layer (e.g. dextrose, starch, polyvinyl alcohol (PVA), among others), which, in turn, is supported on top of a water resistant paper backing. Adhesive layers can be added on top or in between the layered structure to create stronger bonding to surfaces or even to increase durability and resistance to wear and abrasion.

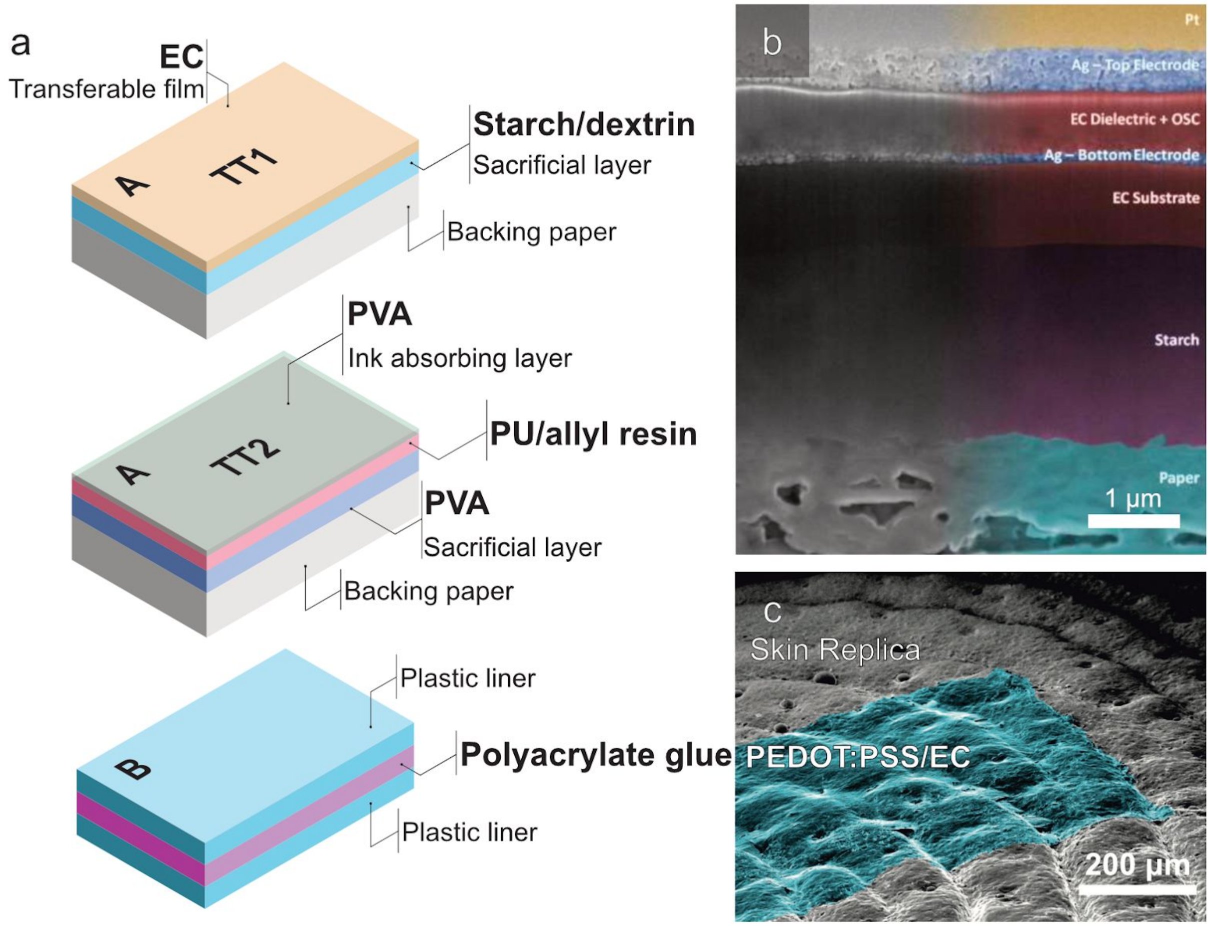

Figure 1. The TT paper (a): water slide decal sheet A – schematics of layers in types TT1 and TT2; adhesive sheet B to be laminated on top of A. (b): scanning electron microscope (SEM) image of a cross section milled by focused ion beam (FIB) of an organic thin film transistor on TT1 paper. The various layers of the substrate (EC, starch/dextrin, paper) as well as the Ag electrodes, the EC dielectric and organic semiconductor are evidenced (reproduced from (27) , with permission by Wiley). (c): colorized SEM micrograph (45° tilted view) of a tattoo (from TT1) transferred onto a silicone replica of human skin (reproduced from (28), with permission by Wiley).

TT paper is a decal specifically designed for transfer on skin and it is available on the market since decades in different formats and compositions. DIY TT kits are composed of two parts: A) water slide decal sheet, B) adhesive sheet (**figure 1**a). DIY TT can be customized by printing an image, typically with laser or inkjet printers, on top of part A.

The adhesive sheet (part B) is usually composed of acrylate glue, which can be safely used in skin-contact applications. This adhesive layer is laminated on top of the decal sheet (part A), right after the image printing. As regards the composition and structure of the decal sheet A, different structures are available by various producers. In our experience with testing TT papers from several suppliers, we have identified at least two main representative structures,[1] schematized in figure 1a. In a first type (TT1) a thin film of ethylcellulose (EC) is acting as the transferable film. Transfer on the skin is possible by dissolution of the intermediate sacrificial layer, composed of starch/dextrin. This layered structure is well visible in the cross section reported in figure 1b, where TT1 is used as a substrate for the fabrication of an OFET for edible electronics.(27) In the second type (TT2) the transferable film is composed of a polyurethane/allyl resin composite plus a topmost (PVA) layer; the role of the latter is to improve wettability and quality of printing. PVA, being readily soluble in water, is also used as an intermediate sacrificial layer.

Despite the availability of these products in commerce, little or no information has been available in literature about their structure (i.e. thickness, surface morphology) and properties (elastic modulus, permeability to moisture, to name a few). The reason probably being the fact that TT paper represented so far a toy or a DIY tool. Just recently it attracted the attention of scientific/technological investigation for application in electronics and wearables. Moreover, even in several cases of scientific publications describing tattoo devices, the proper TT structure is often overlooked. TT paper is just used as a means for transferring a device. However, an insight in the aforementioned

[1] A market available product having TT1 structure is, for example, the Tattoo 2.1 by The Magic Touch, UK, while the TT2 structure is proper of tattoo decal DIY kit supplied by Silhouette America, Inc, US.

features is mandatory to assess the suitability of this unusual substrate for transferable conformable devices.

In **table 1** the thickness and the roughness of the representative TT1 and TT2 papers are reported and compared with those of a medical-grade polyurethane adhesive (MPU). The latter is a conformal adhesive adopted in wound dressing and in some skin-conformable devices.(29,30)

Thickness and roughness are key aspects in selecting a proper substrate for conformable electronics. A thin (nm-µm range) substrate allows for the best conformability to skin and unperceivability (figure 1c).(31) Roughness of a substrate can play a major role in establishing its suitability to thin film devices patterning. Indeed a smooth surface is mandatory in case of thin film deposition, in order to avoid non-uniform coverage, pinholes and defects.

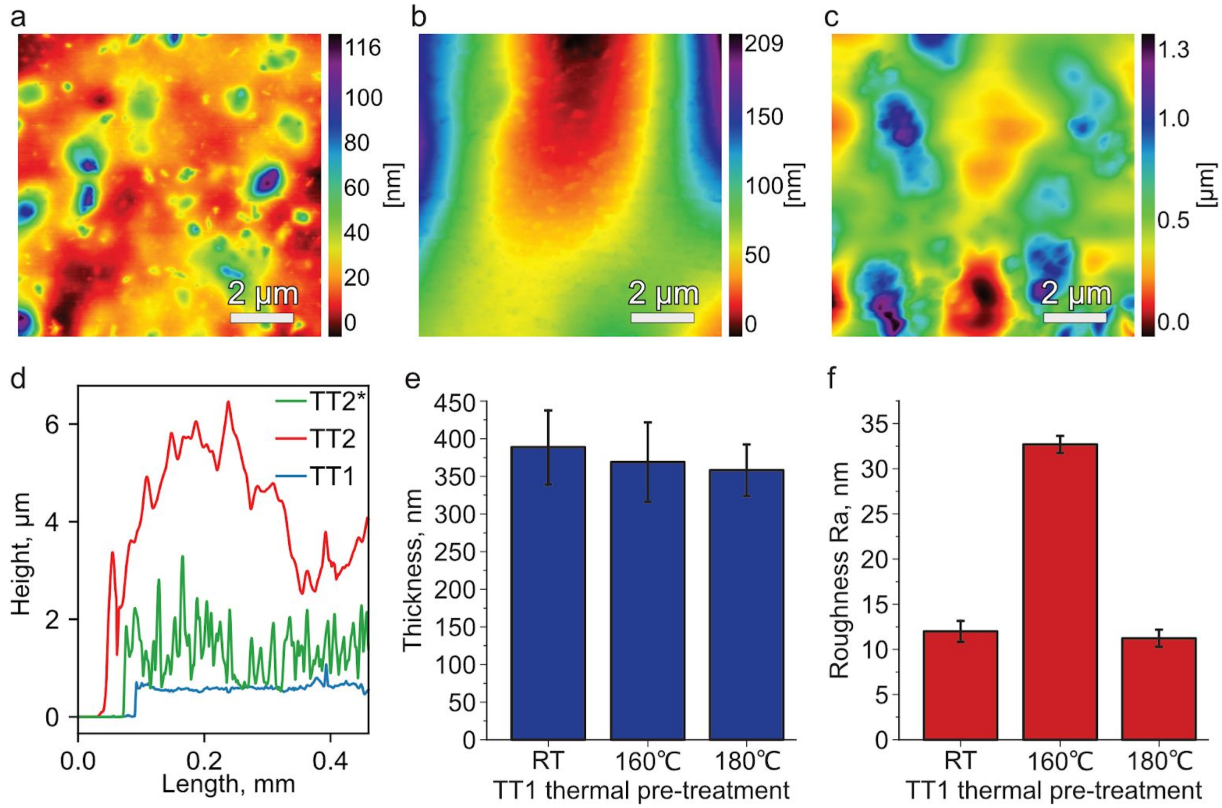

Figure 2. Structure and features of the transfer film from TT paper, (a-c): AFM topography imaging of the film released by TT1 (a), TT2 before (b) and TT2 after water treatment, TT2* (c). Height step profiles of different decal TT papers supported onto Si-wafers as evidenced in stylus profilometry (d). Estimate by AFM of thickness (e) and roughness (f) of TT1 and their variation with thermal treatment. (a-d:adapted from (32) with permission from TU Graz; e,f adapted from Supporting Info of (26) with permission from Wiley).

A comparison of AFM topography imaging of the two substrates permits to highlight the difference among them (**figure 2**a-c). Not only the range of features differ but also their distribution and uniformity.

Table 1. Thickness t and roughness Ra of transfer film from TT1, TT2, TT2* and MPU. TT2*: film released from TT2 after washing with DI water and removal of topmost PVA layer. Thickness as measured by stylus profilometry, roughness as estimated by stylus profilometry and AFM imaging.(32) Values are given as average ± standard deviation.

Transfer Film	Material	t, nm	Ra^a, nm	Ra^b, nm
TT1	EC	608 ± 52	51 ± 26	13 ± 3
TT2	PU/allyl resin + PVA	4400 ± 400	600 ± 250	44 ± 23
TT2*	PU/allyl resin	1460 ± 520	430 ± 100	190 ± 50
MPU	PU + polyacrylate glue	37300 ± 1600 [c]	1800 ± 600	120 ± 50

a: roughness estimation on raw profiles obtained by stylus profilometry (scan length 0.7 mm)
b: roughness estimation as obtained by AFM imaging on 10x10 μm^2 scan operating in tapping mode.

c: overall bilayer thickness, of which: PU ~20 μm, polyacrylate glue ~17 μm.

A first remarkable difference among the two types of TT paper is the thickness of the transferred film, namely the layer which is detached from the paper support when soaked with water. As visible in table 1, the film released by TT1 is the thinnest, having sub-micrometric thickness. TT2 releases a bilayer film of around 4.5 μm overall thickness, with around 1.5 μm PU/allyl resin and around 3 μm of PVA. A comparison of TT1 and TT2 thickness is provided in figure 2d. A similarly striking difference is encountered for roughness (arithmetic average roughness Ra, as estimated at two different length scales by profilometry and AFM imaging, table 1), with the TT1 paper providing the least rough substrate. The obtained values of Ra for TT are considered suitable for most skin-contact electronic applications.

As in any mass manufactured product, differences can be encountered in surface features of TT paper, ascribable to slight variations in the production process. Despite the TT1 thickness was found to be quite homogeneous across sheets and among samples of the same batch (see standard deviation of values in table 1) a remarkable change in thickness among various batches was found. As an example, an average thickness of around 600 nm was found on a batch, while in other batches an average thickness of around 400 nm was reported.(28) Additionally, the surface topography and structure of TT1 was found to vary depending on thermal history, as evidenced by AFM imaging (figure 2 e, f).(26) This was due to known thermal effects related to phase changes in partially crystalline/amorphous EC. Despite some irreversible changes in film structure were observed, the study permitted to assess the feasibility to process the material at temperature up to 180°C, which is relevant for processing required in device fabrication. To summarize, both TT papers are considerably thinner and smoother, in comparison with the MPU reference.

Table 2. Comparison of physical features between four classes of substrates typically used in the field of conformable electronics.

Features	Silicones [a]	PEN (4)	Parylene C (33)	MPU [b]	Tattoo	
					TT1 (26,28)	TT2 (34)
Typ. thickness, μm	100	1 (4)	2 (33)	30 - 55	0.5	1.5
Young's Modulus, MPa	0.025 - 2.5	5000 [c]	2750 [d]	8 - 15	1000	200
Area density, mg cm^{-2}	10	0.14 [c]	0.26 [d]	3	0.05	0.15
Permeability coefficient (water vapour), P_0, g mm m^{-2} d^{-1}atm^{-1}	~1	0.1–4.2 (35,36)	0.08 [d]	33 - 43	440 (37)	NA
WVTR [e], g m^{-2} h^{-1}	~ 0.4	4	1.7	25 - 60	NA (very high)	

a: Various silicone grades (i.e. Ecoflex, Soft Silicon Adhesive, PDMS) at various Young's moduli (see range provided in table) are used in EES.(38) For all other features typical values for the most widely used PDMS 10:1 prepolymer curing agent ratio are considered. Values taken or calculated from (38), unless otherwise specified.
b: Data reported for 2 different market available MPU for skin application: Dellstar EU28 # (SWM Int., data from www.swmintl.com/) and Fixomull Transparent (BSN Medical Gmbh, data from www.bsnmedical.com and (30)).
c: *Goodfellow Polyethylene Naphtalate (PEN) Film properties*, available at www.matweb.com
d: *SCS Parylene Properties*, Specialty Coating System available at https://scscoatings.com

e: Water Vapour Transmission Rate @ T = 37°C for a polymer film at typical thickness specified in table (i.e. typical use in skin-contact devices).

In **table 2** some relevant features of materials, commonly used in conformable electronics, are compared. Despite a comprehensive and detailed study of all the possible substrates for conformable electronics is beyond the scope of this review, table 2 aims to evidence the challenges and opportunities of a tattoo-based approach, in the context of the main approaches reported so far. In particular TT paper is compared with: silicones (e.g. PDMS), typically used in epidermal electronics,(10) PEN and Parylene C, chosen in the so-called imperceptible electronics (39) and various organic bioelectronics applications,(33) and MPU used in some skin-conformable devices.(29,30)

TT paper, PEN and Parylene C exhibit a higher (3 to 5 order of magnitude) Young's modulus than PDMS. Indeed TT paper is not an intrinsic soft and stretchable substrate. Nevertheless, given its ultralow thickness, it is extremely flexible and thus capable to truly adhere as a "second skin", and extend together with skin when this is stretched.

When adhesion on skin is considered further requirements for substrates come into play, apart from surface structure and mechanical properties. Researchers just recently started to address the previously overlooked problem connected with skin perspiration. A relatively thick (tens-hundreds of μm up to around 1 mm, as in many proposed epidermal devices) sheet of silicone or of some thermoplastic material represents a tight barrier against water vapour transpiration, preventing skin breathability.(40) An average Transepidermal Water Loss (TEWL) of 4 - 8 g m^{-2} h^{-1} has been assessed in healthy adult subjects,(41) thus accounting for around 200 - 400 ml/day. An unnatural exchange of the transepidermal water can actually impair the long-term or repeated use of skin-mounted devices, because of moisture and sweat (containing electrolytes) entrapment. This may lead to adverse effects both on end-users and on the device itself. The development of a steady liquid layer can indeed cause skin irritation (e.g. redness, itchiness) as well as damage some devices' components and/or alter its functionality, especially in the case of biomonitoring devices. In order to endow conformable electronics with skin breathability an important parameter to be considered is thus permeability to water vapour, P_0.(37) Values of P_0 listed in table 2 permit to appreciate how different the vapour exchange is for the various kinds of polymeric substrates, with the EC film released by TT1 providing the best permeability and PEN/parylene the worst. However, when skin breathability is considered, one should take into consideration the actual thickness of the polymer membrane. Thus a relevant figure to be considered is the permeability-related Water Vapour Transmission Rate (WVTR), given for the adopted films' thickness. Values of WVTR for the actual polymer membranes used in epidermal applications are not often present in literature, thereafter when not explicitly reported we calculated them from the P_0 by imposing the typical thickness used in application. To assess skin-breathability the WVTR values should be compared with free skin normal water exchange with the ambient, quantified by the average TEWL. A polymer film acts as a barrier against skin transpiration when WVTR $<$ TEWL ~ 5 g m^{-2} h^{-1} . From values of WVTR reported in table 2 it is possible to assess that only TT and MPU films provide good breathability. PEN and Parylene C substrates, despite their very poor permeability but thanks to the adopted reduced thickness, are almost at the limit; silicones do not provide sufficient breathability, unless perforation and porosity are introduced on purpose, as evidenced in various studies.(40) Some recent improvements in terms of silicone breathability came at the cost of increased complexity in fabrication, as the introduction of porosity in the final device assembly.(38)

Stepping apart from skin-mounted conformable sensors, in such applications as photovoltaics and optoelectronics the use of polymer substrates impermeable to water vapour is mandatory. Ultralow values of WVTR are indeed desired in many thin film devices where encapsulation is required to protect the active materials against moisture. The integration of such devices onto skin-mounted conformable electronics, without impairing skin breathability, is a challenging issue not yet solved, with none of the proposed approaches.

As a last remark, every material layer of a skin-worn device contributes to its overall WVTR. Layers of semiconductors or metals act as a tight barrier against water transpiration, given their low permeability. Thus any skin-contact device will have a lower WVTR than just the substrate. In absence of actual experimental data some calculation and modeling for multilayered membranes can provide at least a rough idea and directions for future design of skin-breathable devices.[2] (37)

Overall, the TT paper features reported so far highlight its main features: ultra-conformability and imperceptibility on skin. Mostly due to its low thickness, TT has the ability to establish an intimate interface with the target surfaces (figure 1b), allowing for excellent breathability. Moreover, owing to its layered structure, TT paper is easy to handle. Thus it is a convenient substrate to build-up devices. The manipulation of ultrathin free-standing films can pose critical challenges, as any researcher working on thin-film technology knows. Indeed, they tend to wrap to any surface. This ability is actually what is exploited from their structure, but it represents at the same time a remarkable drawback in terms of handleability. Taking these two considerations together, the most relevant advantage of tattoo paper, in comparison with other

[2] https://www.stevenabbott.co.uk/practical-coatings/permeability.php

substrates adopted in biomonitoring applications, is the possibility to easily fabricate reliable body-compliant and long-lasting devices. The TTs' applications, from the more explored human biomonitoring to the recent edible electronics, will be reviewed in detail in Section 4.

Other unconventional approaches for transferrable electronics can be found in literature, as in the case of water transfer printing (WTP) technology.(42) Here ultrathin patterns can be fabricated on top of a water soluble substrate (i.e. poly(vinyl alcohol) PVA) which get dissolved once the film is released in water. The pattern is then transferred on 3D surfaces through a dipping process. In comparison with the tattoo approach, here the final electronics will have the mechanical features of the sole active material. In WTP the incorporation of serpentines allowed to preserve, after the transfer in water, the electrically conductive pathways without mechanical failure. On the other hand the transferring process in WTP technology is more complex than in tattoo and it requires the help of rigid guides. Thereafter a proper large area coverage with up-scaling capabilities still needs to be proven. Moreover, differently from TT, WTP requires dipping in water of the target object/surface. Another example of unconventional transferable electronics exploits transfer printing through isolated gecko setal arrays.(43) The precise release of microdevices onto unconventional substrates, as a plant, is here performed exploiting the natural geko on/off adhesion property. As in the case of tattoo substrate no glue or high pressure and temperature processes are involved, avoiding any damage to the microdevices, substrates or interfaces.(44) A variety of other contact or non-contact transfer printing techniques have been proposed and demonstrated for the controllable placement of rigid electronic components onto uneven or unconventional substrates for manufacturing of flexible and stretchable devices.(44,45) Another unconventional substrate is silk, adopted passively in biointegrated conformal and biodegradable/bioresorbable electronics. Silk can also be exploited as active elements for flexible electronics, including transistors and memristive devices, as well as conformal biosensors. Silk offers, besides biocompatibility, the advantage of a sustainable production, that is extremely demanded in this green era. Nevertheless fundamental challenges need to be addressed to enable the development of silk-based electronics, as in silk fibroin solution's processability and in microfabrication techniques(46).

Depending on application other properties of TT might be of interest, such as transparency for optoelectronic purposes (solar cells, light detection or communication). Whereas TT1, in our experience, showed more or less complete transmittance (>98 %) in the wavelength range from 350 nm to 900 nm, TT2 transmittance seems to depend on the topmost PVA layer, varying from 40 % to 90 % transmittance. A transparent substrate, together with applications in optoelectronics, would allow the use of optically unperceivable films being suitable for applications in commonly visible areas e.g. face.

A note about drawbacks in using TT substrates has to be made here. Besides not being an intrinsic flexible substrate, TT paper shows a limit in processability for device fabrication. Its layered structure offers indeed only one face to patterning, which prevents the possibility to develop multi-level circuits with via-holes interconnections. Such structural limitation asks more effort at the design level both generally for the arrangement of the device onto one plane and at the level of the external connection. The development of a stable and reliable external connection in conformable electronics is commonly an issue. This aspect is especially challenging when TT is the substrate as the interconnection has to exit the tattoo, without causing a signal loss, and it has to interface a reader, which is typically thicker (at least in the mm-cm range), on the same plane (at the skin interface).

3. Fabrication methods and processing for tattoo-based devices

Key features of skin-conformable and transferable electronics are determined by the balance between skin-like mechanical properties of the carrier while maintaining sufficient electrical conductivity of functional components.(47) Thus, it is important to be able to design and fabricate such devices using the materials and methods that could provide and combine these two factors. Tattoo-based devices have been fabricated with multiple methods, each offering different possibilities. There are two principal approaches for fabrication: vacuum and non-vacuum (solution based) techniques. Vacuum relying methods originate from physical or chemical processes at reduced pressure and usually employ materials deposition via gaseous phase. Thin films and microstructures produced by vacuum methods can have high crystallinity and homogeneity, low surface roughness. The core nature of this family of methods lies in interaction on atomic and molecular level which allows for convenient control of the thickness of the layers. However limited choice of deposited materials and requirement of vacuum (typically high or ultrahigh) vastly increase the cost, scalability and versatility of processing. Therefore a vacuum-based approach is often implemented as a supplement to non-vacuum based technologies. This method family produces thin films from materials in a form of colloidal solutions – inks, sols, gels, pastes or emulsions. This approach is easy-scalable and can be performed at ambient conditions. Since the key material is dispersed in a solution medium, it is important to carefully choose the solvent. Some solvents could negatively affect the transferability of TT. While water is usually a safe medium, usage of organic solvents, for instance in the case of EC in TT1 paper, like tetrahydrofuran, chloroform, ethanol, toluene and ethyl acetate should be chosen carefully.(48)

One of the most common techniques is screen printing, especially for printed electronics,(49,50) sensors,(51,52) and microfluidics.(53) In contrast to others non-vacuum deposition methods the physics of the process is very simple. It is a cheap and scalable process which relies on the transfer of material onto a substrate. Desired material in a form of highly viscous ink (500-10000 cP) is delivered through a stretched mask with a fine mesh in a moment of contact with a substrate induced by applied pressure (**figure 3**a).

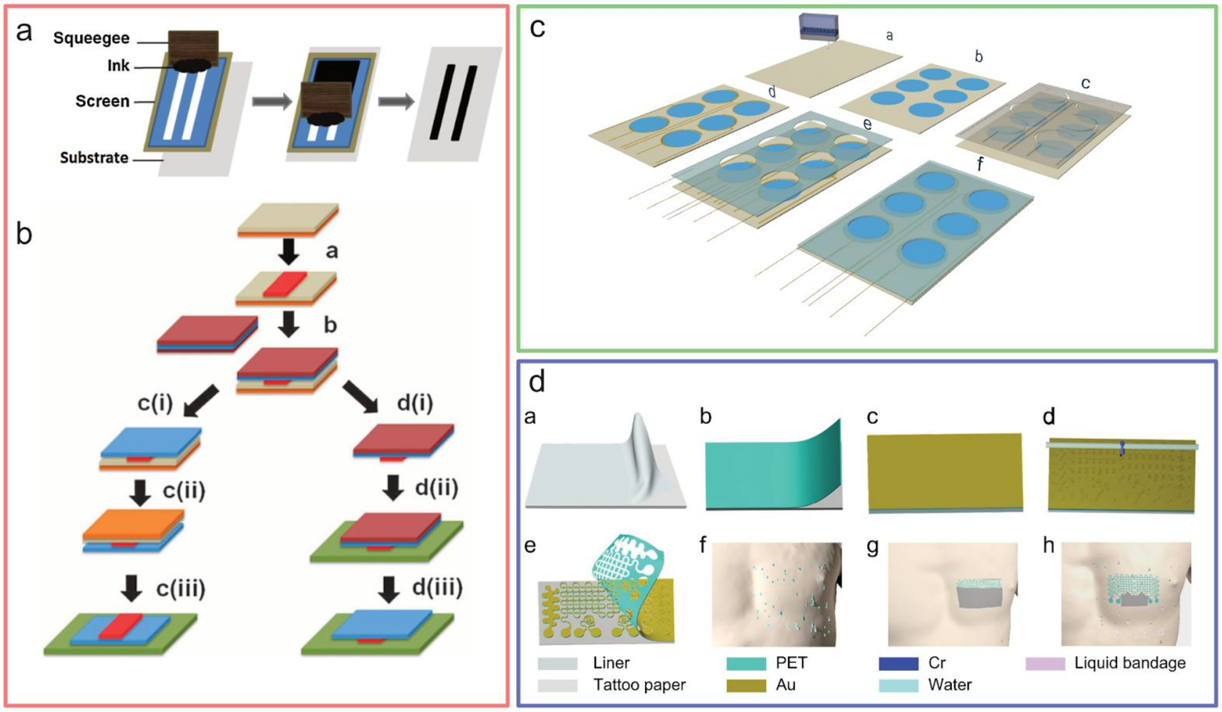

Figure 3. Fabrication processes on TT. (a): screen printing process (picture reproduced from (52) with permission from Elsevier). (b): Schematics of the screen printing process for electrochemical device fabrication (reproduced from (54) with permission by Royal Society of Chemistry). (c): schematic view of TT multielectrode array fabrication by inkjet printing and sputtering (reproduced from (28) with permission by Wiley). (d): cut-and-paste fabrication process of "e-tattoo" (reproduced from (55) with permission by NPJ).

The first example of screen printed tattoo-based device was an electrochemical sensor proposed in 2012 by Wang's group.(54) Fabrication procedure included subsequent printing of working, reference and counter electrodes (figure 3b). Working and counter electrodes were usually made of carbon inks, while for the reference electrode Ag/AgCl inks were used. Further, a thin insulating layer was added to facilitate the release of the tattoo prior to the deposition of printed electrodes.(56) Screen printing of electrochemical devices is attractive owing to the simplicity of the technology and to the ease of customization. Sensitivity and selectivity of the sensors can be adjusted by the addition of supplementary electrodes and by working electrode functionalization. Drop casting of Nafion™ and electroplating of bismuth film for trace metal detection,(57) or deposition of Prussian blue for monitoring of ethanol or glucose in sweat have been proved.(58,59) In later works the reference electrode performance was improved by using composite mixture of Ag/AgCl ink with carbon fibers or by adding NaCl/KCl saturated gel layer, to reinforce mechanical stability and to enhance the conductivity.(60) Another example of screen printed tattoo-based electrochemical devices are biofuel cells and batteries.(61) In this case negative and positive printed carbon electrodes are functionalized by electrodepositing of metals from their salt solutions.(62)

Screen printed tattoo-based films have also been used to overcome limitations in electronic components assembly linked to traditional lamination and direct printing methodologies. Piva et al. adopted a printed PEDOT:PSS on TT as a charge selective electrode for photovoltaic cell.(63) The electrode can be directly transferred onto the developed organic solar cell just by wetting the support paper. Such process eliminates the need in surface treatment and the use of ink additives, which are often harmful for the other active layers, while maintaining good conductivity (R_{sheet} = 170 Ω) and power conversion efficiency (up to 7 %).

Screen printing on TT is also widely used for fabrication of sensors for electrophysiological monitoring. Recently, Hanein's group demonstrated screen printed conductive carbon electrodes with plasma polymerized 3,4-ethylenedioxythiophene (pPEDOT) on TT for surface electromyography recordings.(64) The electrodes design has been lately improved by the use of a silver ink for the feed lines, while the carbon ink was adopted only for the skin-contact sites.(65) In another work,(66) the silver elastomeric tattoo plus the adhesive porous layer (ca. 36 μm thick) was compared with a screen-printed silver ink tattoo (ca. 11 μm thick) providing increased yield strain (ca. 8% vs. 4%) and lower Young modulus (ca. 0.03 MPa vs. 0.27 MPa).

Screen printing is a powerful, simple, highly scalable method for the deposition of functional layers. However, it has some drawbacks related to the development of conformable electronics, mainlythe need of highly viscous inks, typically more than several thousands of cP. The high ink viscosity has two main consequences. First, polymer binders, organic solvents, and other additives have to be added to the ink to reach the optimal texture, limiting the content of the target component and inhibiting its key electrical, optical and mechanical properties. Second, the thickness of the printed layers depends on the nature of the used inks, mainly from the dimensions of the dispersed phase which are usually in the order of several micrometers. Screen printing is a contact manufacturing process that requires the use of a mask, which is usually expensive by itself and causes waste of material. Another drawback of this contact printing method, related to the need of a master, is the relatively poor lateral resolution, mostly limited by the mask mesh size. In some extreme cases, with a combination of the right screen material, mesh size, correct exposure of the emulsion, optimal surface energy, and suitable inks it is possible to reach the individual feature size as low as 40-60 μm, while in general cases it is 100-500 μm.(67,68)

A more advanced printing technology is inkjet printing, which is based on digital and non-contact transfer of material in a form of colloid onto a substrate. In comparison to screen printing, inkjet does not require a physically patterned mask for printing and allows producing more complex features with resolution of down to 10 μm and submicrometer thickness.(69) Inkjet printing can be effectively combined with other patterning technologies. Zucca et al. firstly implemented inkjet printing along with spin-coating as a supplemental fabrication method.(26) Spin coated PEDOT:PSS films were patterned into electrodes by inkjet printing a sodium hypochlorite (NaClO) solution. NaClO acts as an overoxidizing agent which causes irreversible breaking of conjugation in PEDOT. Local treatment of thin PEDOT:PSS film leads to formation of large area electrodes separated by insulating borders. Hanein's group also used inkjet printing of PEDOT inks for coating of screen-printed silver/carbon electrodes observing a reduced skin-contact impedance.(70) Inkjet printing could be successfully employed not only as an assistive processing step, but also as a direct additive approach for thin film deposition. Ferrari et al. demonstrated fully printed PEDOT:PSS multielectrode arrays for electrophysiological monitoring.(28) Vacuum sputtering of gold was also here adopted to create thin interconnections between printed PEDOT:PSS electrodes and connection pads for external measurement devices (figure 3c). Bonacchini et al. inkjet printed all components of edible organic field effect transistors directly on untreated commercial tattoo paper.(27) After each printing step the thermal postprocessing at 125 °C was applied for solvent removal and sintering of AgNP inks.

Tavakoli et al.(71) showed a non-conventional approach of conductive traces fabrication using printed silver nanoparticles (AgNP) ink covered with gallium-indium eutectic solution (EGaIn). The AgNP circuit was inkjet printed, while a thin layer of EGaIn was drop casted on top, filling the gaps between nanoparticles. In that way traces with improved conductivity and more tolerant to tensile strain were produced. Excess of EGaIn was removed by a weak solution of acetic acid acting as a reducing agent and rinsed with water afterwards. For mechanical protection final circuits were encapsulated with a PDMS film. In further work by the same group laser printing was used for circuits templating, letting toner also be the wetting layer for silver epoxy paste which adheres only to the printed toner part.(72) EGaIn was deposited on top of wet silver nanoparticles resulting in a semisolid layer which exhibited high electrical conductivity and low electromechanical coupling.

A different approach that does not entail direct patterning of materials, has also been reported. Wet transfer, dry patterning strategy" for graphene electronic tattoo (GET) fabrication was proposed.(73) The so called "cut-and-paste" method implemented chemical vapor deposition of graphene on a Cu substrate on top of which polymethylmethacrylate (PMMA) was spin-coated. Cu was etched leaving graphene embedded into soft thin (≅ 400 nm) PMMA matrix which was then transferred onto TT paper. PMMA/Graphene layer was patterned by cutting with a mechanical plotter allowing to peel off excess area. Same group has also shown alternative approach of tattoo-based electronics by sequential thermal evaporation of Cr and Au on 1.4 μm PET film laminated on slightly wet tattoo paper.(55) Figure 3d displays fabricated electrodes with open-mesh serpentine ribbon shape which helped sustain mechanical deformation at large strain.

4. Applications

4.1 Human Biomonitoring

Tattoo-based devices find their main application in non-invasive human biomonitoring. The possibility to pattern functional materials onto tattoo paper has been investigated in the last 10 years, with the most recent scenario in imperceptible wearables development. Seamless skin-conformable devices will be able to improve the user experience while providing continuous high-quality health data for remote biomonitoring.

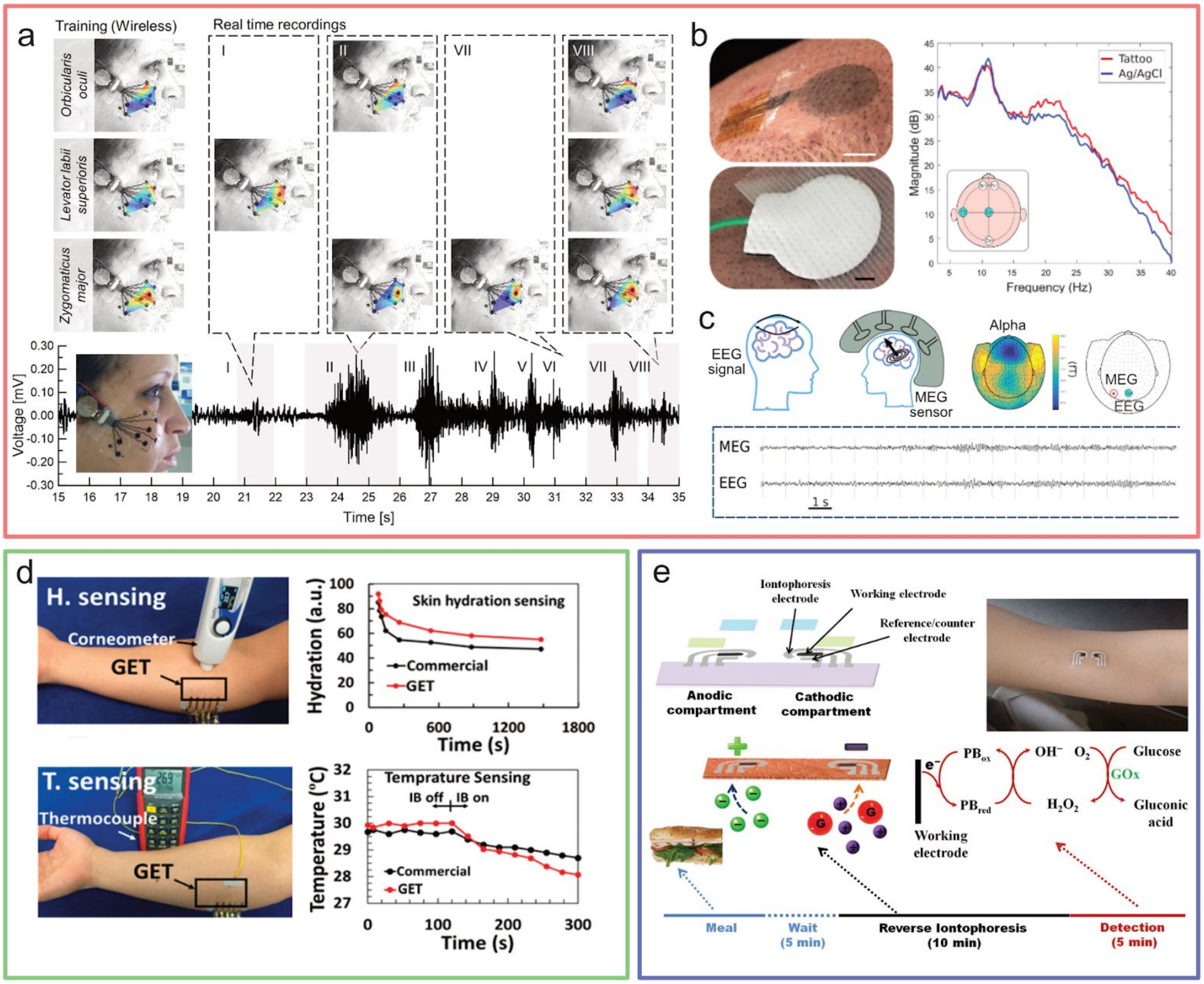

Figure 4. Tattoo-based human biomonitoring. (a): wireless fEMG recordings. In the upper part (real-time recording and training boxes) the independent component analysis (ICA) maps, where red color indicates highest muscle activation. Independent component (IC) maps were calculated for EMG segments I (1.3 s), II (3 s), VII (1.8 s) and VIII (1 s) (picture reproduced and adapted from (74) with permission from Springer Nature). (b,c): temporary tattoo electrodes (TTEs) in clinical electro- and magneto-encephalography. (b): the power spectral density of EEG recordings performed with TTEs in comparison with standard Ag/AgCl electrodes. (c): schematization of EEG and MEG recordings with the MEG map showing no interferences of TTEs electrodes and the contemporary EEG-MEG signal acquisitions (b,c adapted from (34) with permission from NPJ). (d): GET device in the hydration (H. sensing) and skin temperature (T. sensing) assessment in comparison with commercial sensing devices (reproduced from (73) with permission by American Chemical Society). (e): tattoo-based electrochemical sensing for a non-invasive glucose monitoring. The electrodes design, the skin-transferred device and the operation mechanism combining reverse iontophoretic extraction of interstitial glucose and an enzyme-based

amperometric biosensor (reproduced from (58) with permission by American Chemical Society).

Among various biosensing applications, biopotential monitoring is one of the most investigated. Surface electrophysiology recordings indeed represent essential tools for basic research, diagnostic and monitoring purposes in clinics, or in sport science as well as in neural engineering. These recordings include signals acquisition techniques like electroencephalography (EEG), electromyography (EMG), electrocardiography (ECG). Non-invasive interfacing with the body for biosignal acquisition is the preferred approach, as accomplished by means of dedicated skin-contact electrodes.(75) Dry (metal) or wet (gelled Ag/AgCl) electrodes are typically used.(76) Ag/AgCl electrodes are today the gold standard owing to their high signal quality. The main drawbacks of state of art skin-contact electrodes are related to their intrinsic bulkiness, weight, lack of compliance and obtrusiveness when worn on skin, among others. Additionally, wet Ag/Agcl electrodes suffer from gel drying out in about 6-8 hours, impairing their continuous or long term use. In contrast, tattoo based electrodes have been presented that can overcome the aforementioned limitations. As recently demonstrated, biopotential sensing enabled by tattoo-based sensors can produce the best signal-to-noise ratio (SNR), in comparison with other soft and stretchable electrodes.(77) These results have been attributed to a larger contact area developed by the tattoo electrodes, with respect to the other stretchable sensors, owing to their conformal contact . Tattoo electrodes (based on TT1 paper) for the recording of biopotentials have been firstly reported in 2015 by Zucca et. al who demonstrated the acquisition of surface electromyography (sEMG) and used it for the myographic control a robot arm prosthesis.(78) A thin spin coated or inkjet printed film of the conducting polymer poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS) was used as electrode. With just around 600 nm of overall thickness these tattoo electrodes represented the thinnest skin-contact electrodes until then. Moreover, thanks to the excellent conformability, adhesion on skin was solely provided by means of VdW forces, without the use of any glue.

Following that first report, the fabrication process and the reliability of temporary tattoo electrodes (TTEs) have been improved and single as well as multielectrodes arrays (MEAs) have been developed for the recording of various biosignals.(28,34) TTEs long-term recording capability has been assessed over more than 48h. ECG and EMG signals were recorded from diverse anatomical locations showing the benefits of these ultraconformable electrodes also in the field of facial EMG (fEMG).(28) This is quite relevant since the lack of an optimal electrode is limiting the growing of fEMG and its applications in multiple areas as video gaming, lie detection, neurological diseases evaluation and monitoring of facial motion disorders. Indeed, bulky and cumbersome Ag/AgCl electrodes are not suitable to this purpose, as they impair the user's natural movement.

Additionally, growing of facial hair through TTE has been demonstrated without impairment of functionality,(28) which opens up interesting and unprecedented opportunities in long term monitoring in body locations densely covered by hair (e.g. shaved scalp).

Usage of TTEs on skin for multiple days evidenced excellent breathability with no adverse side effects as itchiness, redness or accumulation of epidermal perspiration, as shown in other cases.

Tattoo electrodes for fEMG (based on a commercial TT paper, by Papilio, having a structure similar to TT1 but releasing a thicker film) have also been developed for the recording of freely behaving humans.(74) Here, fEMG electrodes were adopted, in wired and wireless mode, to detect the three muscles involved in different smiles (the *orbicularis oculi*, the *zygomaticus major*, and the *levator labii superioris* muscles). With the wireless setup, coupled with an independent component analysis (ICA) algorithm, the activation of the three muscles was identified in face-to-face interactions, in a natural work environment (**figure 4a**). Notably, in this case the overall electrode thickness was ~70 μm, thus preventing a conformal contact with the complex texture of skin, characterised by 10-100 μm thick valleys and ridges. Nevertheless, the device features (e.g. the dry electrodes patterned on the DIY TT kit and the ICA algorithms) enables minimal mechanical artifacts and high-spatial resolution with electrodes crosstalk-free mapping, that are not possible today in clinical practice with standard electrodes. On the same strategy fEMG tattoo electrodes arrays were proved to achieve muscle localization, targeting anatomically distant muscles on the lower and upper part of the face.(70) Subject-specific muscle mapping, for both voluntary and spontaneous smiling, was also achieved with an hemifacial 16 electrodes array, showing an automated and objective assessment of normal and abnormal smiling with applications in neuropsychological diagnosis as well as in facial plastic surgery.(79) ECG and EEG recordings, performed using GET sensor fabricated with “cut-and-paste” method, were proved with comparable performances with respect to gold standard gel electrodes.(73) In addition to electrophysiological measurements, the GET was also able to measure skin temperature and hydration (figure 4d). Lately GET electrodes have also been adopted to acquire electrooculography (EOG) signals for human-robot interfaces.(80)

Among biopotential monitoring, the EEG recording is the current frontier and the most critical to be performed with new conformable electrodes. This is mainly because of EEG small signal amplitude and the low frequencies content. EEG signals range from 0.5 to 100 μV in amplitude, which is about 100 times lower than ECG signals, with frequency content from 0.1 to 100 Hz. Moreover, there is the need to develop long lasting devices in order to enable long-term and continuous brain monitoring, especially with application in the neurocognitive field (e.g. epilepsy) and in neuroprosthetics. The development of conformable and unperceivable EEG electrodes can have groundbreaking consequences, as the use of brain neural computer interfaces (BNCIs) in daily life scenarios (as described in (81)) could get more realistic.

EEG recordings have been demonstrated and characterised by means of TTEs (based on TT2* paper) in a clinical monitoring set-up (figure 4b,c). Full compatibility with complementary instrumentation adopted for neurocognitive evaluations, as the magnetoencephalography (MEG), was proved for the first time with dry tattoo electrodes.(34)

A different example of tattoo sensing platform for skin physiology monitoring is based on screen-printed elastomeric silver electrodes plus a porous adhesive layer.(66) The elastomeric nature of these electrodes and the porous layer were here adopted to develop an improved mechanical contact with the skin, in terms of strain and adhesion. ECG tattoo electrodes have also been developed with a capacitive coupling (e.g. not in direct contact), using a top adhesive layer and proving their usability up to five days.(82)

The most recent advance in tattoo-based wearables proposes a battery-free platform, with a wireless energy harvesting system, for the recording of human ECG.(83) The platform is composed of a tattoo-based unit built on TT2 paper and an ECG reader. The tattoo unit (thickness from 7 to 105 μm, depending on printing strategy – inkjet or screen printing – without the insulating plastic covering) is produced by printing a stretchable AgInGa circuit and it is composed of two electrodes for electrophysiological recording and a coil for energy harvesting. The reusable ECG circuit, able to acquire and transmit the heart rate, is composed of a Bluetooth modulus and a single-channel integrated biopotential chip. The platform has been tested on one healthy volunteer demonstrating "data-on-demand" transmission of the heart beat rate. Excellent SNR was proved, thanks to the bi-phasic AgInGa conductor. Future directions will investigate the biocompatibility of the active material, the EGaIn liquid metal, that still needs to be fully proved and the capability of continuous monitoring.

4.2 Electrochemical biosensing

While the development of imperceptible wearables for electrophysiology is the most contemporary scenario, the first application of tattoo paper in human monitoring has been in electrochemical sensing, as pioneered by Wang's group(54). They exploited the capability of TT to develop an intimate contact with the skin to have direct access to chemical constituents in the sweat for real-time health and fitness monitoring. From an analytical point of view, one of the major barriers to monitoring the concentration of ions in sweat lies in the sampling step (e.g. Macroduct® sweat collection systems for sodium estimation). Many different TT electrochemical sensors have been demonstrated embedding a working, a reference and a counter (when needed) electrode. In the case of lactate monitoring the amperometric biosensor exploited an enzymatic mediator onto the working electrode,(84) and sweat lactate analysis was successfully demonstrated during exercise. With the same strategy a stripping-voltammetric Zn detection has been proved for determination of trace metals in sweat.(57) Monitoring of pH was also proved, by means of ion-selective electrodes (ISEs), on multiple locations of the human body. The potentiometric sensors, evaluated during exercise, showed stable signals even under profuse perspiration.(85) With a similar approach ammonium has been monitored, using an ammonium-selective polymeric membrane, and a polyvinyl butyral (PVB) solid-state reference membrane was proved for the first time in a wearable device.(56) The same group further presented a tattoo-based potentiometric sodium sensor with Bluetooth signal transmission.(86) Thereafter, an epidermal glucose monitoring device has been developed which combines both extraction and sensing operations. The device couples reverse iontophoretic operation and an amperometric biosensor (figure 4e). It has two compartments, an anodic and a cathodic one, between which a small current is applied in order to extract (on the cathode) the skin interstitial fluid (ISF) containing glucose. Through the cathode working electrode, modified with the glucose oxidase (GOx) enzyme, micromolar levels of glucose were recorded, also in the presence of other common interfering chemical species, demonstrating high selectivity and sensitivity.(58) With the same approach, a wireless alcohol monitoring platform has been developed. Here iontophoresis interests transdermal delivery of pilocarpine to induce sweat and the working electrode is functionalized with an alcohol-oxidase enzyme.(59) Subsequently, simultaneous sampling and analysis of the two biofluids is demonstrated. The concept is realized through sweat stimulation (via transdermal pilocarpine) at anode, alongside extraction of ISF at cathode.(87) On a similar concept a wearable for chemical-electrophysiological sensing has also been reported, where lactate and bipolar ECG were measured simultaneously, with negligible cross-talk, enabling a new class of hybrid sensing devices.(88) Finally, ultrasound transdermal microballistic delivery, based on microporous membranes containing cargo-loaded “microcannons”, has been reported with possible application in penetrative needle-free drug delivery for therapeutics and skin care.(89)

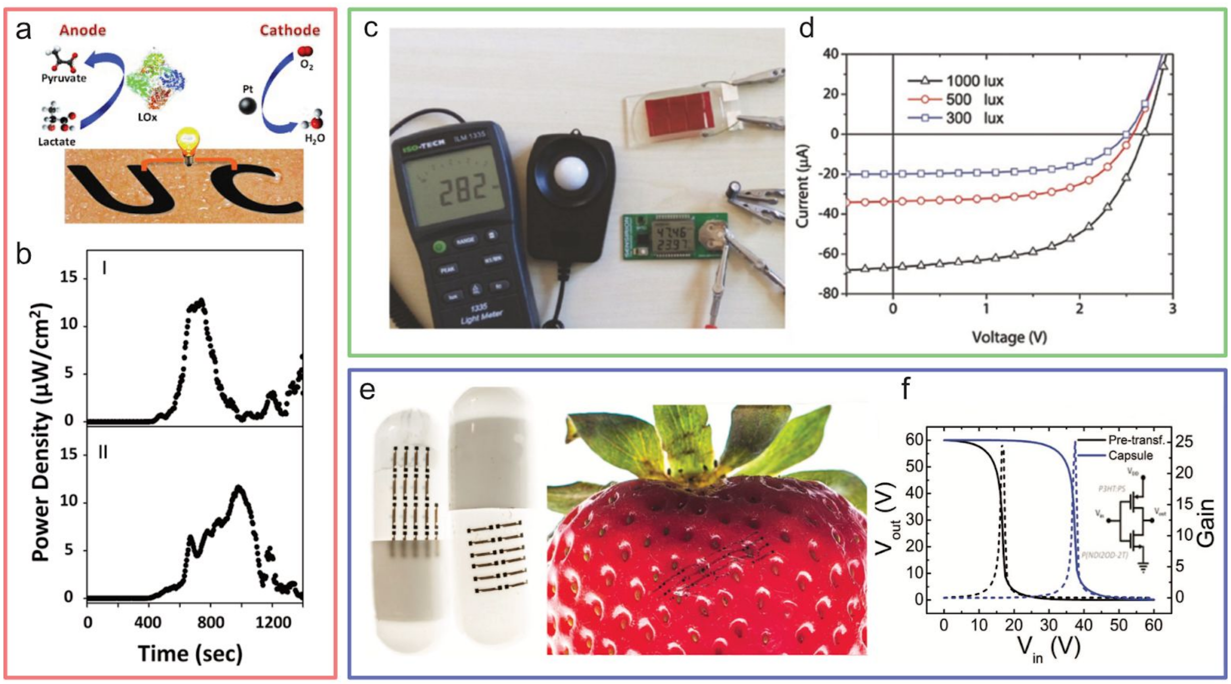

Figure 5. Tattoo-based electronics, beyond skin applications. (a) Schematics of a tattoo biofuel cell, functionalized with lactate oxidase (LOx), to harvest biochemical energy from human perspiration. (b) Power density generated and recorded with the biofuel cell from human sweat in real-life scenario. Repeated on-skin measurements with a single biofuel cell: I) first measurement, II) measurement after 2 h (a,b reproduced from (90) with permission by Wiley). (c) A tattoo-based charge selective electrode for organic indoor photovoltaics. The photovoltaics minimodule (active area 6 cm^2) coupled with a backup capacitor powering a temperature–humidity sensor and an LCD display in indoor conditions (≈280 lux). (d) I–V curves of the photovoltaics minimodule measured at 300, 500, and 1000 lux (c,d reproduced from (63) with permission by Wiley). (e) Tattoo-based edible electronics transferred onto a capsule and a strawberry. (f) The

voltage transfer curve (VTC) and gain curve of a tattoo complementary inverter based on P3HT:PS and P(NDI2OD-2T) organic semiconductors, acquired before (black) and after (blue) transfer on a pharmaceutical capsule (e,f reproduced from (27) with permission by Wiley).

In all these tattoo biosensors extensive in-vitro characterization has been performed revealing in most cases a near-Nernstian trend response, with fast and reversible reactions between the sensor and the analyte solution. Particular attention has been also devoted to the mechanical characterization, proving that such electrochemical TT sensors can endure repetitive deformations and mechanical strains onto different body-area both during exercise and normal daily activity. Notably, in the case of potentiometric sensors, the tattoos functionality has been maintained even when minor cracks were observed in the electrodes. This is due to the fact that potentiometric response is independent of electrode area, in contrast to voltammetric and amperometric measurements.(85)

4.3 On-skin energy harvesting and batteries

Tattoo paper has been also adopted as the substrate for the fabrication of wearable powering modules. An enzymatic biofuel cell (BFC) was developed that can harvest energy from lactate, a metabolite secreted on skin during perspiration.(90) The BFC operation was based on the oxidation of sweat lactate and the reduction of oxygen at the anodic and cathodic compartments (**figure 5**a). The relatively low and variable power output (from 5 to 70 μW cm^{-2} depending on individuals different fitness levels) indicates that more efforts are still required in the power generation and for the integration of energy storage components, to propel BFC as a new paradigm within tattoo electronics.(90)

On the other hand, a Ag-Zn tattoo battery has been developed and used to power a LED when worn on skin. The tattoo battery displayed limited cycling capabilities (charge–discharging efficiency) and capacity losses, imputed to the fabrication process, including electrode architecture and types of electrolytes. Nevertheless in the route of thin-film batteries Ag-Zn cells provide an attractive alternative to Li-ion batteries because of the extensive global reserves of Zn and because they are safer (Ag–Zn cells use water-based electrolytes, unlike Li-ion batteries rely on hazardous nonaqueous solvents).(62)

4.4 Beyond skin applications

A more exotic application of tattoo paper has been proposed by Piva *et. al.* for the fabrication of organic indoor photovoltaics (figure 5b).(63) The idea was to use the tattoo paper as a transferable and transparent carrier of the charge selective electrode. A PEDOT:PSS layer was screen-printed onto the tattoo paper and then directly transferred onto the photoactive layer. The excellent transmittance of TT1 permitted to achieve the goal of transferring a robust yet semi-transparent top electrode onto glass-supported organic photovoltaics With this approach an excellent power conversion efficiency (PCE) as high as 7%, from 300 to 1000 lux was achieved and a real indoor application was proved powering a temperature–humidity sensor with its LCD display in an office environment (250-300 lux).

Another class of devices that can be fabricated onto tattoo paper are transistors, which are the fundamental building blocks in electronics, especially for signal elaboration. In a recent work tattoo paper (TT1) served as a versatile platform for applications in edible electronics.(27) Fully printed organic field-effect transistors (both p- and n-type) were successfully transferred and operated onto food and pharmaceutical capsules proving the integration of electronics onto ingestible substrates with complex geometries (figure 5c).

Finally, the possibility to build wireless communication modules onto tattoo paper has been reported. Screen printed tattoos has been characterized with respect to a relatively low sheet resistance (41 mΩ/sq), giving hope for the development of high-frequency components, as antennas that can be used in wireless applications, such as remote healthcare.(91)

5. Conclusions

TT paper has been shown as a suitable and affordable substrate to develop conformable electronics. Conformable devices have to answer two big challenges. First, they have to provide an imperceptible interface with the surface, acting as a second-skin on it. Second, they should ensure reliable manipulation and transferring of the devices, which can be difficult when high aspect ratio (thickness/lateral dimension ~ 10^{-4} – 10^{-5}) comes into play.(19) TT paper fulfills these requirements owing to its layered structure that allows for easy release of an ultrathin film. Multiple fabrication strategies can be adapted to work on TT paper, including various printing methods (e.g. screen printing, inkjet) physical and chemical vapour deposition. The possibility to pattern TT with diverse methodologies open to heterogeneous applications. Since its inception in the field of human biomonitoring, around ten years ago, TT has been adopted in numerous studies with multiple purposes, primarily within on-skin applications. Lately TT paper has been coupled with standard electronics to build up wearable and wireless platforms.(59,65,83) The fabrication of wireless devices with biomonitoring purposes exploits today a hybrid approach, which couples a tattoo-based sensing unit with a standard signal processing/transmission unit (based on rigid, mm-thick, Si-based electronics,). The combination of thin-film sensing devices with flexible electronics circuits can be envisioned in future developments. These coupling could allow to have a reusable flexible processing/transmission unit and a low-cost disposable tattoo sensing interface. Such an approach can open new paradigms in diagnosis and monitoring of human health, introducing continuous, cheap and non-invasive opportunities. The coupling however comes at the cost of some new challenges to be overcome as regards the mechanical coupling of the ultrathin disposable tattoo with the thicker and stiffer flexible unit.

Nevertheless, the long-term challenge will be the integration of multiple sensors and electronic subsystems on TT (e.g. circuits for signal conditioning/transmission and powering) for the development of a fully functional conformable electronic device. A specific challenge in this respect will be connected with compatibility of multiple consecutive deposition and fabrication processes on the same tattoo paper substrate.

Apart from skin-contact applications, TT paper has been adopted as an unconventional substrate for devices in edible electronics and photovoltaics. Recently, a self-healing transistor has also been proposed. It is a 3 μm thick tattoo-like sensor assessed for on-body detection of temperature and humidity.(92) The self-healing capability has been here integrated to lead to more environmentally friendly applications.

Along this direction TT paper can enable new opportunities for the rise of diverse and contemporary fields. The first example is in the area of sustainable and transient electronics.(20,21) TT exhibits a low environmental footprint, owing to its materials composition and production methods. Moreover, its ultralow cost makes it an ideal candidate for the fabrication of transient sensors that can be safely degraded in the environment after deployment. Some future directions can be envisioned in environmental, plants and crop monitoring, as recently shown for other conformable sensing technologies in so-called “plants wearables”.(2,3) Here, the prominent capability of TT to be perforated without losing its integrity and functionality, and to allow for excellent moisture exchange could open novel opportunities for monitoring plants during their growth with minimal obtrusiveness.

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